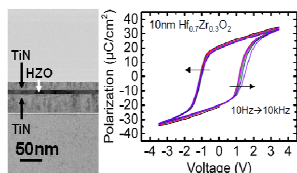


A First-Principles Study on Ferroelectric Phase Formation of Si-Doped HfO_2 through Nucleation and Phase Transition in Thermal Process

Background and Motivation



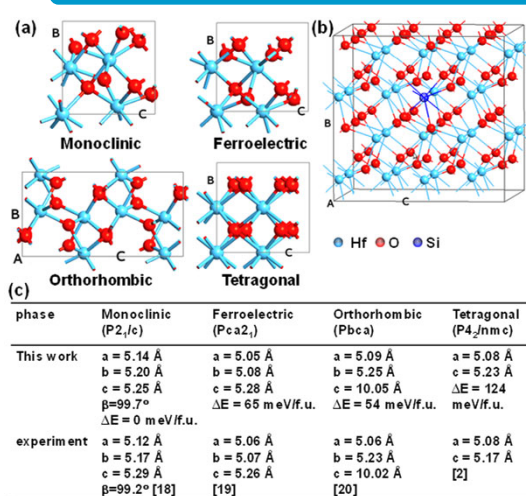
M. Kobayashi et al., J. EDS 2018



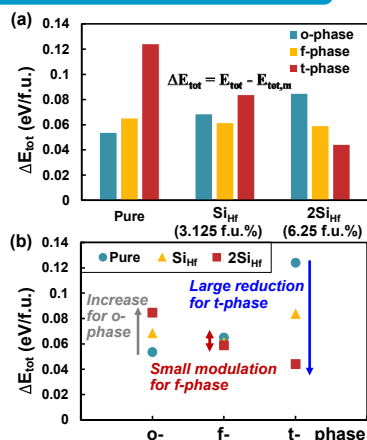
- Ferroelectric- HfO_2 (FE- HfO_2) is an emerging CMOS compatible material which opens new opportunities of next generation transistor and memory technologies for IoT applications.
- Classical nucleation and growth theory give new sights in ferroelectric phase formation of HfO_2 . The mechanism of ferroelectric phase formation of HfO_2 is still in debate. Especially, discussion on the effect of kinetics is rare in the previous reports.

Objectives: further understanding of ferroelectric phase formation of pure and Si-doped HfO_2 through the whole process from fundamental thermodynamics and kinetics study based on first-principles simulation.

Atomic Structures and Si-dopant



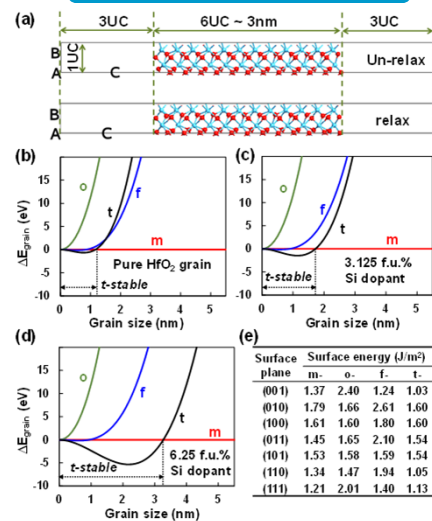
- The lattice is almost consistent with the previous experimental reports for all phases.



Total energy modulation with Si-dopant

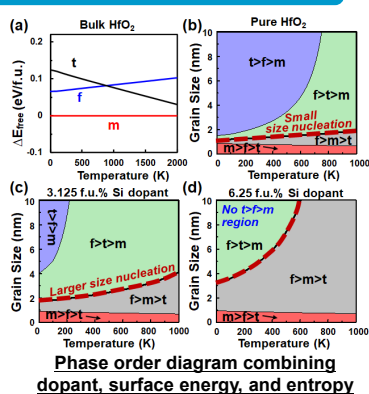
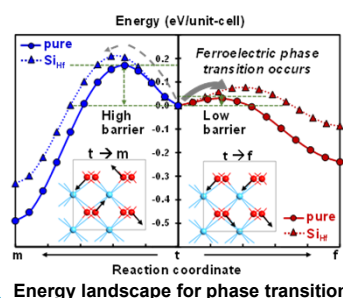
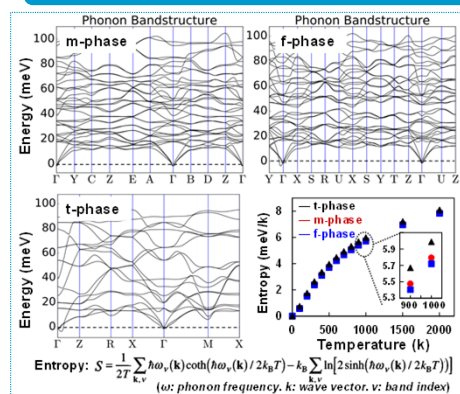
- Dopants mainly affect the relative energy of the t-phase and have quite small effect on the f-phase. The m-phase is still the most stable phase with dopants.

Surface Energy

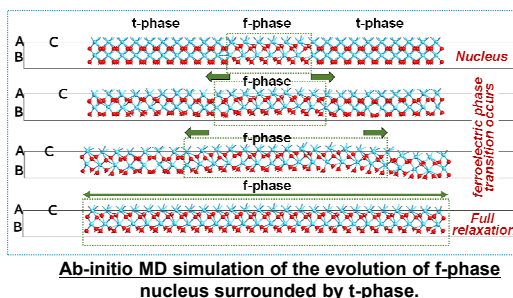


- With surface energy, the t-phase can be the most stable phase in small grain size.

Phase Order Diagram and Phase Transition

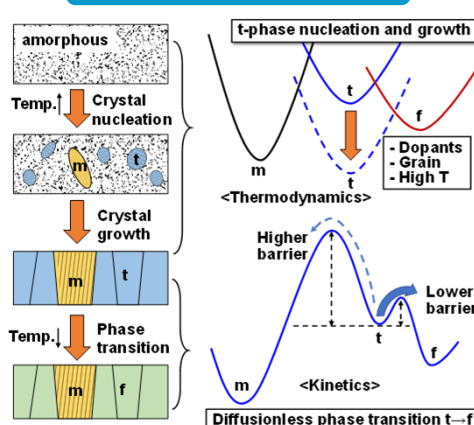


Phase order diagram combining dopant, surface energy, and entropy



Ab-initio MD simulation of the evolution of f-phase nucleus surrounded by t-phase.

Summary



- 1) The t-phase can be thermodynamically preferable at the initial nucleation process with the effect of dopants and surface energy at high temperature. With grain size increase and temperature decrease, the diffusionless $t \rightarrow f$ phase transition could happen which has the lower activation barrier than the $t \rightarrow m$ transition.
- 2) Si-dopants play important roles both in the nucleation and phase transition process. Doping concentration should be carefully controlled to obtain the ferroelectric HfO_2 film.

This work was supported by JST SICORP, JSPS KAKENHI, and KIOXIA research funding.